NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

EARTH RESOURCES SURVEY PROGRAM

TECHNICAL LETTER NASA-100

ULTRAVIOLET ABSORPTION AND LUMINESCENCE STUDIES

PROGRESS REPORT FOR THE PERIOD
APRIL TO DECEMBER 1967

By

William R. Hemphill
U. S. Geological Survey
Washington, D. C.

January 1968

Prepared by the Geological Survey for the
National Aeronautics and Space Administration (NASA)
under NASA Contract No. R-146-(09-020-006)

MANAGEMENT
REPORT

MANNED SPACECRAFT CENTER
HOUSTON, TEXAS

UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
WASHINGTON, D.C. 20242

Interagency Report
NASA-100
January 1968

Mr. Robert Porter
Acting Program Chief
Earth Resources Survey
Code SAR - NASA Headquarters
Washington, D.C. 20546

Dear Mr. Porter:

Transmitted herewith is one copy of:

INTERAGENCY REPORT NASA-100

ULTRAVIOLET ABSORPTION AND LUMINESCENCE STUDIES

PROGRESS REPORT FOR THE PERIOD FROM APRIL TO DECEMBER 1967*

by

William R. Hemphill**

The U.S. Geological Survey has released this report in open files. Copies are available for consultation in the Geological Survey Libraries, 1033 GSA Building, Washington, D.C. 20242; Building 25, Federal Center, Denver, Colorado 80225; 345 Middlefield Road, Menlo Park, California 94025; and 601 East Cedar Avenue, Flagstaff, Arizona 86001.

Sincerely yours,

William A. Fischer
Research Coordinator
Earth Orbiter Program

*Work performed under NASA Contract No. R-146-09-020-006
**U.S. Geological Survey, Denver, Colorado

UNITED STATES

DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

INTERAGENCY REPORT NASA-100

ULTRAVIOLET ABSORPTION AND LUMINESCENCE STUDIES

PROGRESS REPORT FOR THE PERIOD FROM APRIL TO DECEMBER 1967*

by

William R. Hemphill**

January 1968

Prepared by the Geological Survey
for the National Aeronautics and
Space Administration (NASA)

---

*Work performed under NASA Contract No. R-146-09-020-006

**U.S. Geological Survey, Washington, D.C.

9.1267

CONTENTS

Appendices

U. S. GOVERNMENT PRINTING OFFICE : 1959 O - 511171
867-100

ILLUSTRATIONS

Figure 1. Excitation and emission spectra of Rhodamine B. After spectrofluorometric analysis furnished by G. K. Turner Associates, Palo Alto, Calif.

2. Profile of the D_2 Fraunhofer line of sodium, and adjacent absorption lines and continum (Minnaert, etal, 1940).

3. Schematic diagram showing optical and electronic components in the conceptual design of the Fraunhofer line-discriminator.

4. Curves showing spectral transmission of assorted ultraviolet and visible filters, and the quantum efficiency of the S-13 photo-cathode.

5. Curves showing the quantum efficiencies of the cesium-telluride and cesium-antimony photocathodes, and the spectral transmission of a Corning 7-54 filter.

6. Curves showing diffuse spectral reflectance of phosphate rocks.

7. Curves showing diffuse spectral reflectance of limestone samples.

8. Curves showing diffuse spectral reflectance of andesite samples.

9. Curves showing diffuse spectral reflectance of rhyolite samples.

10. Curves showing ultraviolet excited luminescence emission from three phosphate rocks and a calcite reference.

11. Curves showing ultraviolet excited emission from three limestone samples and a calcite sample.

12. Curves showing combined spectral reflectance and luminescence intensities between 1000Å and 3000Å.

ULTRAVIOLET ABSORPTION AND LUMINESCENCE STUDIES: PROGRESS REPORT FOR THE PERIOD FROM APRIL TO DECEMBER, 1967.

By

William R. Hemphill

U. S. Geological Survey

INTRODUCTION

Ultraviolet studies were formally set up as a U. S. Geological Survey project in November, 1965 and have been sponsored jointly by both the Survey and by the National Aeronautics and Space Administration (NASA) since that time. The objectives of the project are fourfold: (1) to determine the ultraviolet absorption and emission properties of selected natural materials, (2) to evaluate these properties in terms of their identification or discrimination value, (3) to design and construct appropriate instrumentation to perform these identification and discrimination functions, initially from close range and later from aircraft and spacecraft; and (4) to assess the results.

This report summarizes work undertaken during the nine month period from April 1 to December 30, 1967 and covered by NASA contract PO-65757-G. This work was concentrated in the following areas:

1. Conceptual and detailed designs, and fabrication of a suitable instrument for detecting luminescing materials against a daytime solar background.
2. Evaluation of the limitations of existing ultraviolet-visible line scan imagers, and possible advantages of alternative systems.
3. Laboratory measurements of the ultraviolet and visible reflectance and luminescence of selected rocks and minerals.

FRAUNHOFER LINE-DISCRIMINATOR

General Statement

The so-called "method of line-depths" was originally suggested and successfully used by astronomers as a means to detect luminescence of lunar surface features against a high solar background (Grainger and Ring, in Kopal, 1962). This method involves observing the ratio between the central intensity of a selected Fraunhofer line and the continuum as reflected from the lunar surface, and comparing it to the same ratio in the solar spectrum directly. Luminescence is indicated where the ratio in the lunar spectrum exceeds its solar conjugate.

The feasibility of using this method and a Fraunhofer line-discriminator to detect luminescence of geologic materials on the earth's surface during daylight was suggested in a series of laboratory experiments by Betz (1966). Betz successfully detected luminescent samples of calcite, phosphate rock, and colemanite with a grating spectrometer, using the solar ultraviolet as an excitation source. Despite the poor atmospheric conditions in the Chicago area where the experiments were performed, these experiments indicated the severe optical inefficiency of the grating spectrometer, and demonstrated the need for a field-test prototype, suitable for later optional modification for use in an aircraft. Such a device was believed to be within the state-of-the-art.

Preparatory to issuing a Request-for-proposal, a Statement-of-work (Appendix A), describing the operational requirements of a Fraunhofer line-discriminator (FLD) was prepared by the Geological Survey and submitted to NASA. This Statement-of-work emphasized the following:

1. The prototype instrument was to be designed to detect Rhodamine B dye in water in concentrations of 20ppb or less. Rhodamine B (fig. 1) is a luminescent dye used by hydrologists and oceanographers to monitor current dynamics in rivers and estuaries. Rhodamine B was selected because this material would lend itself ideally to quantitative testing of the proposed instrument. Moreover, conventional methods of monitoring this dye are extremely laborous and awkward; it was believed that if this semi-automated line-depth method was successful, it would be of immediate practical benefit in dye studies.
2. Design of the prototype was to permit one instrument to function initially as a laboratory and on-the-ground field instrument. Later, if so indicated, the design

was to permit modification of the same instrument to a form suitable for testing from an aircraft. This arrangement would permit design refinements to be made as testing proceeds. Thus, features such as automated data handling, which would be redundant or unnecessarily complicated during preliminary laboratory and field testing, would not be added until the flight evaluation phase, at which time design requirements would be better defined.

3. Although the prototype was to be specifically for detection of Rhodamine B, the design was to be sufficiently versatile so that pending successful completion of the dye tracing tests, the instrument could be modified to operate in other spectral regions in order to evaluate its application in detecting luminescing materials other than Rhodamine B.

4. Final acceptance of the prototype instrument from the contractor would be based upon demonstrating detection of Rhodamine B in concentrations of 20ppb or less from

a distance of 500 feet with a field-of-view of one degree.

The Request-for-proposal was issued April 18, 1967 by the Manned Spacecraft Center (MSC) Houston. Proposals received by the deadline on May 18, or within one week after the deadline were evaluated and graded by a committee composed of personnel from both NASA and the Geological Survey. The winning contender was the Perkin-Elmer (PE) Corporation of Norwalk, Connecticut.

Further negotiations were conducted by the Perkin-Elmer Corporation and MSC; contract NAS 9-7447 was formally signed August 9, 1967. In addition to the design and construction of the instrument, the agreement provides for completion of all acceptance tests and delivery of the Fraunhofer line-discriminator (FLD) by January 12, 1968. A complete project schedule is shown in Appendix B.

Conceptual design

The emission peak of Rhodamine B is near 5800Å (fig. 1) and accordingly, the nearby D_2 Fraunhofer line (fig. 2) of sodium is the most appropriate line to be resolved by the Fraunhofer line-discriminator.

The key components of the Perkin-Elmer design are two glass-spacer Fabry-Perot filters with a half-width of less than 0.7Å and a peak transmission of more than 50 per cent. This extremely narrow bandwidth and high peak transmission represents a state-of-the-art advance in filter fabrication. For detection of Rhodamine B, the transmission peak of one filter will be at the central intensity of the sodium D_2 line; the transmission peak of the other filter will be centered several Angstroms distant at a convenient point on the solar continuum adjacent to the D_2 line. Low noise photomultipliers are located behind each filter (fig. 3). A system of lenses, beamsplitters, and choppers permit the instrument to "look" alternately downward at the ground target, and upward toward the sun, and to monitor the ratio of the central intensity to the continuum in each look. An analog computer will compare the two ratios and convert any difference that may be present into a signal which is proportional to the amount of luminescence in the ground target. The signal will be displayed on either an A-scope or a strip-chart

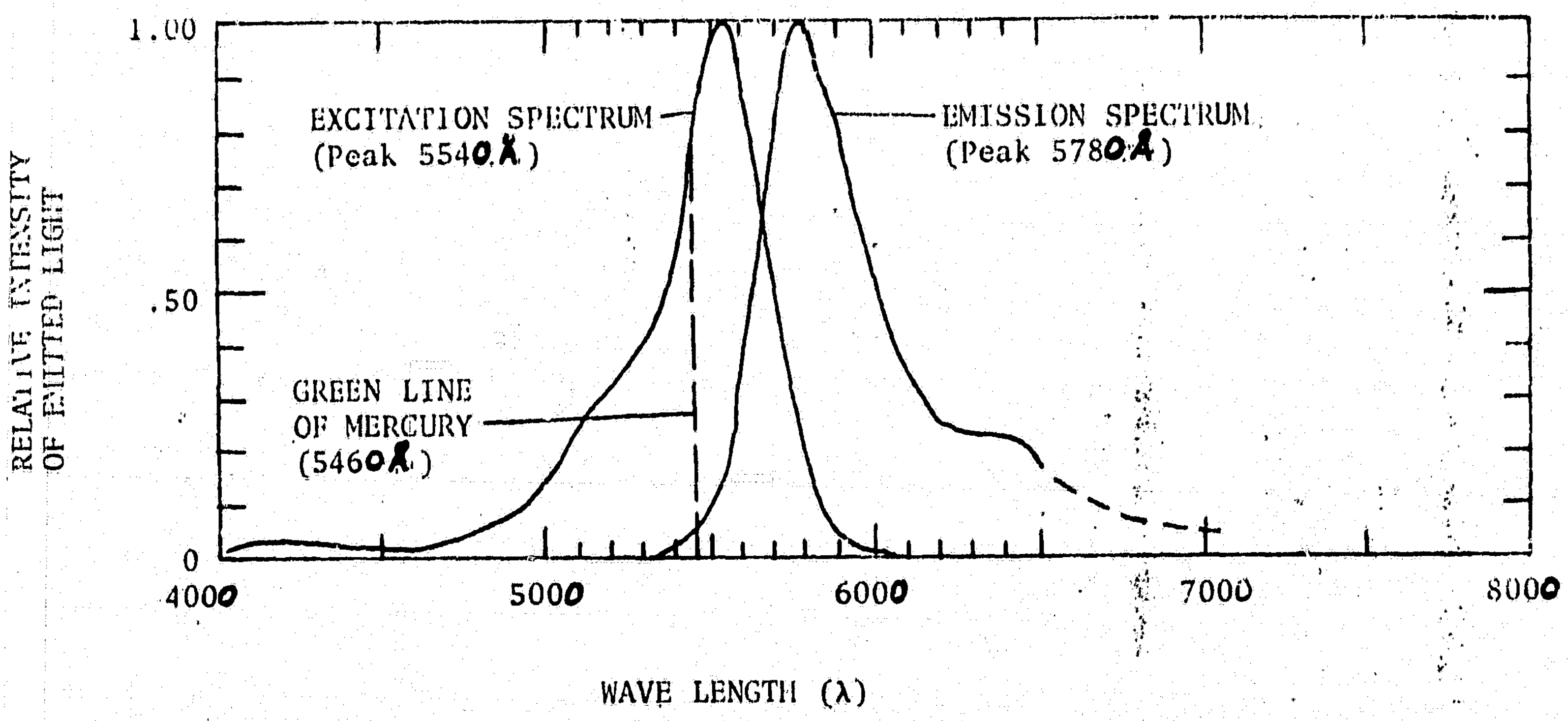


Figure 1. -- Excitation and emission spectra of Rhodamine B. After spectrofluorometric analysis furnished by G. K. Turner Associates, Palo Alto, Calif.

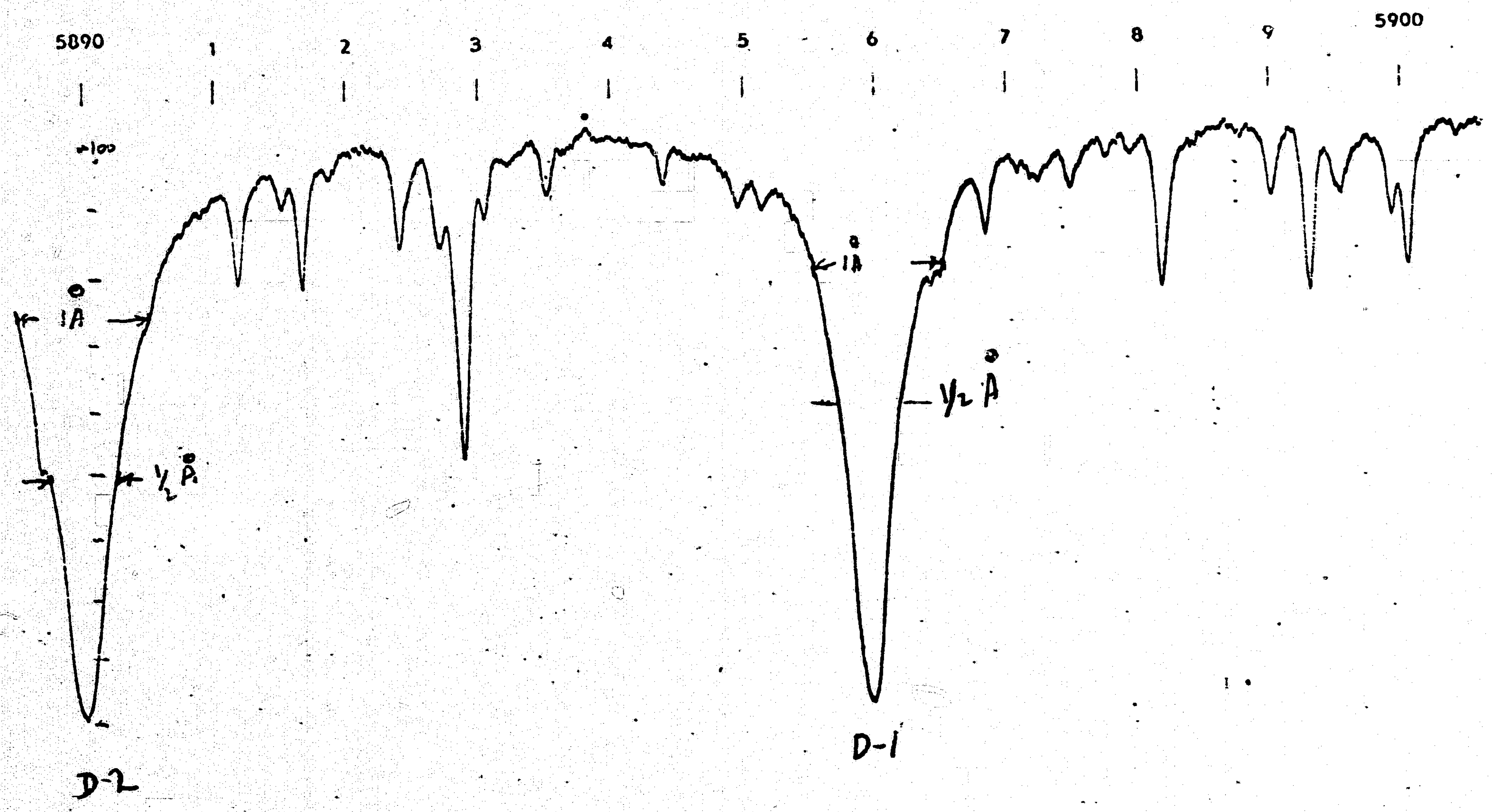


Figure 2. Profile of the D_2 Fraunhofer line of sodium, and adjacent absorption lines and continuum (Minnaert, etal, 1940).

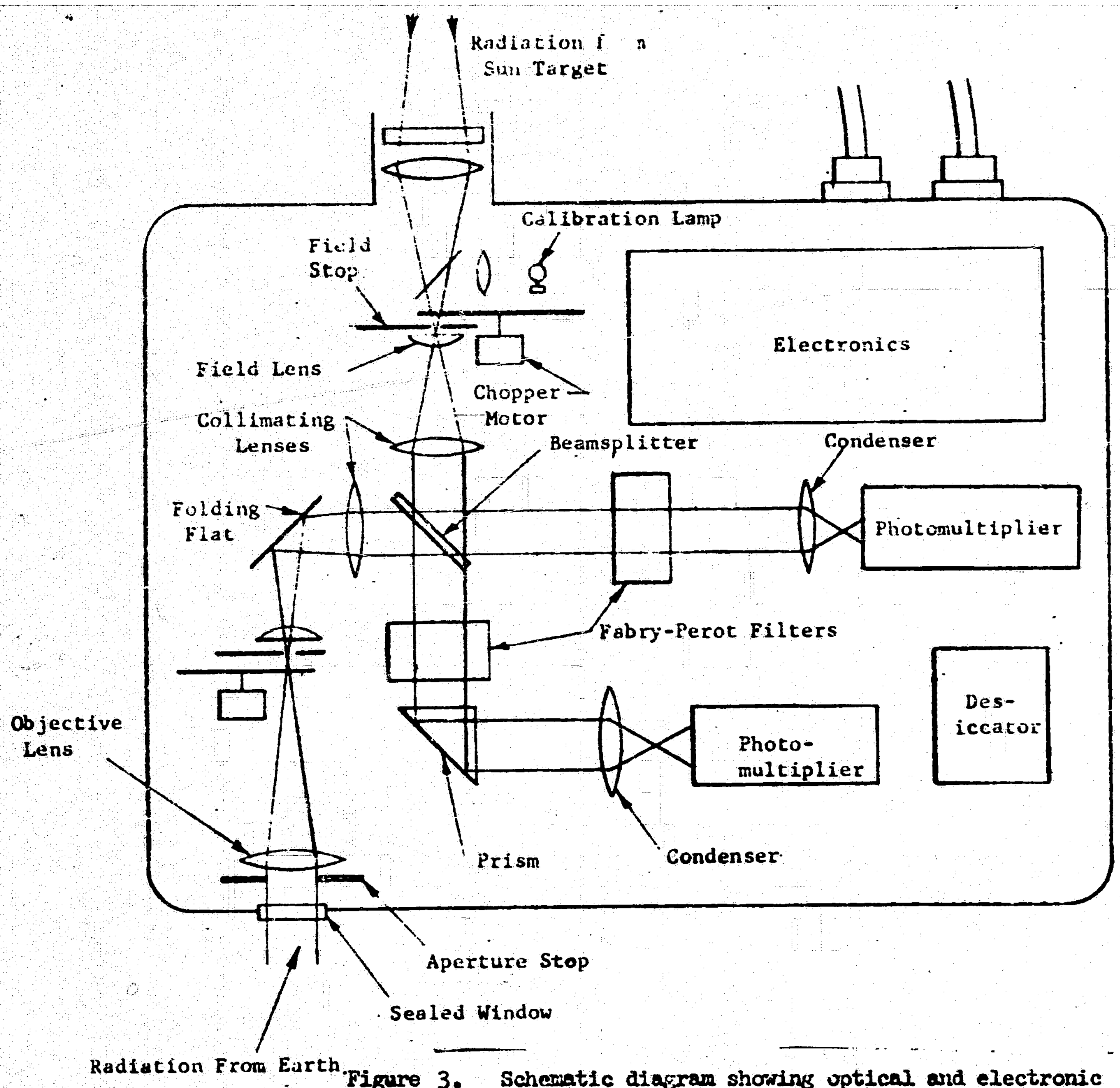


Figure 3. Schematic diagram showing optical and electronic components in the conceptual design of the Fraunhofer line-discriminator. (Courtesy of the Perkin-Elmer Corp.)

recorder whereon luminescence intensity will be plotted as a function of time.

Plans for future work

The Perkin-Elmer Corporation is scheduled to deliver the Fraunhofer line-discriminator on or before January 12, 1968. Trials will be conducted at the Geological Survey's Water Resources Laboratory in Phoenix, Arizona and will test the ability of the instrument to detect Rhodamine B dye in fresh water in concentration of 20ppb or less from a real or simulated distance of 500 feet. Initial tests will be static on-the-ground tests, but if indicated, further tests will be conducted from low-flying aircraft.

Modifications are tentatively planned to permit the instrument to detect luminescence of other materials, such as phosphate rock, water surface oil slicks, and chlorophyll a; however, these modifications are dependent upon successful completion of the Rhodamine B tests.

INSTRUMENT EVALUATION STUDIES

Rhodamine B detection system

Betz (in review) discusses alternative methods for daytime airborne monitoring of Rhodamine B dye in streams and estuaries. These methods include photography, filter photometry, and the Fraunhofer line-depth method.

Ichiye and Plutchak, (1966) used aerial photographs to identify dye clouds in waters adjacent to Long Island. The photographs were taken through a filter which permitted transmission of only those wavelengths longer than 5600Å; this is the spectral region where the emission and reflectance spectra of Rhodamine B are at maximum. Dye areas of greatest concentration are the brightest on the film. A microdensitometer was used to relate film sensitivity and exposure to the vertically integrated concentration of the dye in the water. Betz (in review) calculates that the dye would be readily detectable for concentrations of 30ppb to a depth of 10 meters, but it is questionable whether these depths would be integrated by a photographic system unless the water was exceptionally clear. Water absorption in the yellow-red region increases with wavelength, and where water is turbid, suspended material may also absorb or scatter both the emission and the excitation radiation. Photographic contrast will thus be minimized where gross reflectance properties of the suspended material are similar to the combined emission and reflectance spectra of the dye. The detectability of the dye is definitely marginal at concentrations of 30ppb or less at integrated depths of one meter.

The filter photometer discussed by Betz (in review) consists of two boresighted optical systems, each having an interference filter, a lens, an aperature defining a one-degree field of view, and a detector. The filter for one system permits transmission of only these wavelengths at and near the emission peak of Rhodamine B (Fig. 1); the filter for the other system would permit transmission in a spectral regional where Rhodamine B emission is low or non-existent (5200Å, for example). Luminescence would be detected by comparing the ambient signals at 5800Å and at 5200Å. Although signal-to-noise would be about one order of magnitude better than other methods considered, the filter photometer would not be capable of distinguishing between Rhodamine B emission and spectra of comparable wavelength reflected from either suspended material in the water or from the bottom. (The filter photometer would also be ineffective in distinghishing luminescing minerals and rocks, which ordinarily must be detected against a heterogeneous background.)

The principle of the Fraunhofer line-depth method and the operation of a Fraunhofer line-discriminator are described in a previous section of this report (see p. 3). Compared with photography and filter photometry, line depth method would be

U. S. GOVERNMENT PRINTING OFFICE : 1959 O - 511171
867-100

the only technique capable of distinguishing emission of the Rhodamine B dye from radiation reflected from the bottom or scattered by material in suspension. The line-discriminator is the only device that theoretically could be applied to detection of a variety of luminescing materials against both homogeneous backgrounds such as water, and against varied spectral backgrounds, such as a rock outcrop. Betz (in review) considers the line-depth measurement to be particularily applicable in detecting low concentrations of Rhadamine B dye ($<$ 30ppb), although he points out that wave glitter--specular reflectance of the sun--within the field of view would greatly increase the reflectance component of the signal and thereby render comparatively small luminescence values ($<$ 30ppb Rhodamine B) undetectable. However, this glitter effect over water targets could be minimized by deliberately orienting flight lines and the instrument in directions away from surface glitter.

Red and infrared leakage of ultraviolet filters

Airborne line-scanners have been used to detect and image ultraviolet light reflected from the earth's surface adjacent to the aircraft ground track. The photomultiplier detectors are equipped with filters designed to reject the visible part of the spectrum and transmit only the ultraviolet. Unfortunately, ultraviolet filters leak red and infrared light at wavelengths longer than 6500A, a spectral region where conventional

U. S. GOVERNMENT PRINTING OFFICE : 1959 O - 511171
867-100

photomultipliers retain marginal sensitivity. In order to determine the significance of the unwanted signal in the ultraviolet line-scan imagery, a series of experiments were performed by the University of Michigan's Willow Run Laboratories using four ultraviolet filters furnished by the U. S. Geological Survey. The transmission of each filter is shown in figure 4.

The filter marked "33 peak" is a metal dielectric filter with a 100Å half-width peaking at 3300Å. The filter marked " 33" is also a dielectric filter with a sharp long-wave cut-off at 3300Å. The Corning 7-60 and 7-37 filters are broad-band filters transmitting ultraviolet and absorbing most visible light.

The measurements were conducted with the University of Michigan's modified AN/AAS-5 scanner equipped with an Amperex 150 UVP photomultiplier and an S-13 response (fig. 4). Each filter was mounted between a .010 inch aperture and the photomultiplier faceplate. The scanner was located about five feet above a fiberfrax surface two feet square. Fiberfrax is a reflectance standard with high reflectance values in both the near ultraviolet (3000Å) and visible regions of the spectrum. The fiberfrax was illuminated by the sun at an angle of 25 to 30 degrees from the normal. The sky was partly covered by well-defined clouds, but measurements were made only when the sun was clear.

Figure 4. Curves showing spectral transmission of assorted ultraviolet and visible filters, and the quantum efficiency of the S-13 photo-cathode.

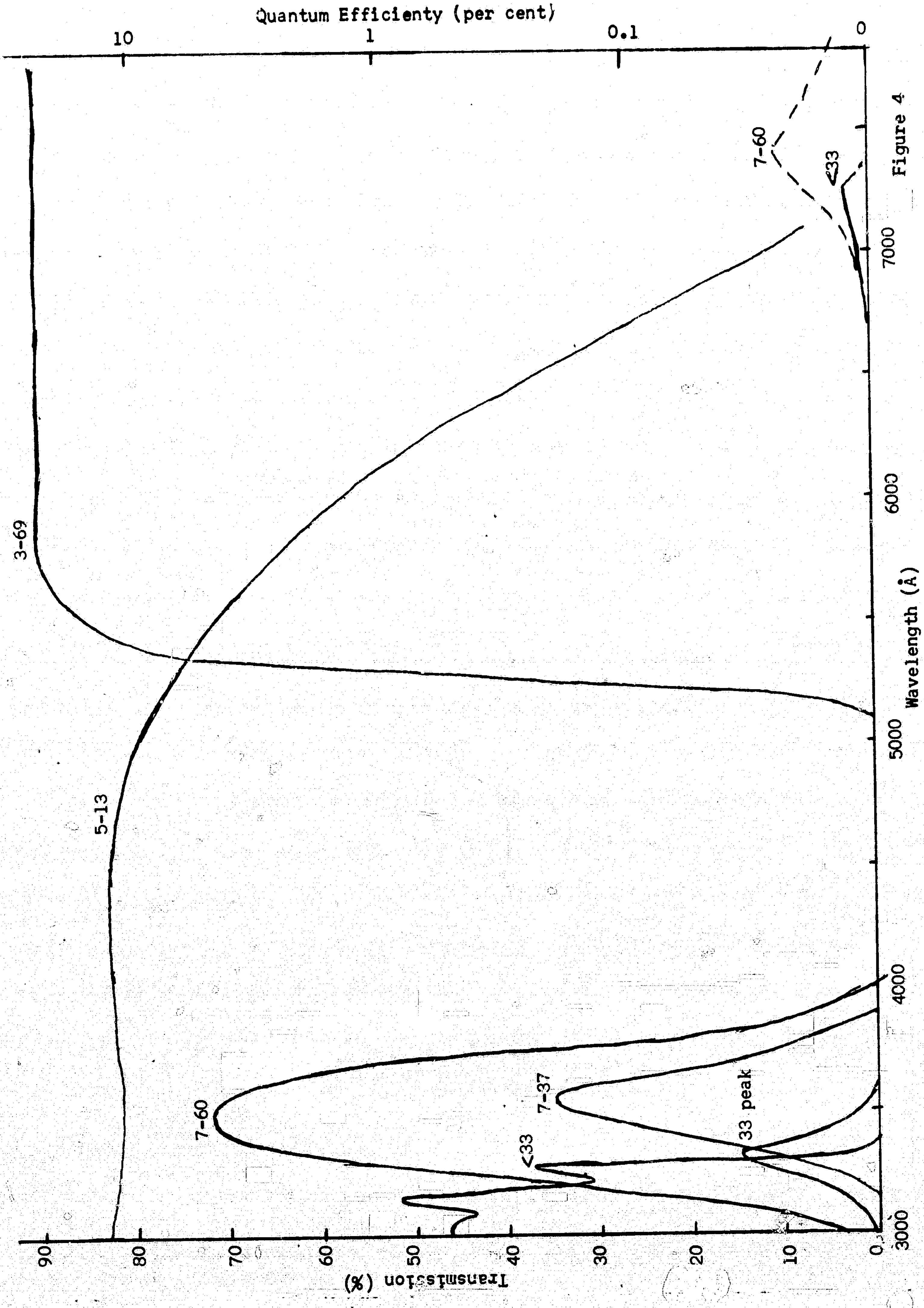

Quantum Efficienty (per cent)
10
1
0.1
0
Transmission (%)
90
80
70
60
50
40
30
20
10
0
Wavelength (Å)
3000
4000
5000
6000
7000
3-69
5-13
7-60
<33
7-37
33 peak
7-60
<33

Figure 4

The photomultiplier output was measured and recorded for each ultraviolet filter. The measurement was then repeated with each filter used in combination with a Corning 3-69 filter (fig. 4). The Corning 3-69 blocks essentially all ultraviolet light, but has a red and infrared transmission that exceeds 80 percent. Thus, any signal detected from the filter combination could be attributed to red leakage of the ultraviolet filter.

Results of the test indicate that between five and 11 percent of the light transmitted by the two dielectric filters and detected by the photomultiplier is due to leakage in the red and infrared band. Leakage of the Corning 7-60 ranges between 14 and 19 percent, but leakage is less than 0.1 percent for the Corning 7-37.

Red-infrared leakage is within tolerable limits only with the Corning 7-37 filter. Flight tests are planned using the Corning 7-37 in combination with other ultraviolet filters such as the metal-dielectric "K33" filter. The Corning 7-37 will function as a red-infrared blocking filter. Although this additional blocking will also severely reduce the ultraviolet, this is the only filter system capable of reducing red leakage to tolerable limits.

U. S. GOVERNMENT PRINTING OFFICE : 1959 O - 511171
867-100

Comparison of photomultiplier-equipped line-scanners and image orthicon ultraviolet imaging systems.

Ultraviolet-sensitive photomultipliers have been installed in airborne line-scanners and used by the University of Michigan Willow Run Laboratories, and other organizations to detect ultraviolet light (> 3000Å) which is reflected from the earth's surface adjacent to the aircraft's ground track. A spinning mirror permits the swath to be scanned from side to side so that all elements in the swath are covered, element by element, line by line. Lateral coverage is thus provided by the spinning mirror; forward coverage is provided by the forward travel of the aircraft. Detected energy is printed out in film strips which show the two-dimensional positions of the UV reflecting objects in the ground swath.

Standard UV photomultipliers, such as the S-13 and S-5 (fig. 4 and 5) have a high sensitivity in the visible region of the spectrum, and although ultraviolet filters such as the Corning 7-60 (fig. 4) and 7-54 (fig. 5) have been used to reject visible light, all ultraviolet transmitting filters also "leak" light at wavelengths longer than 6700Å (see p. 14). As discussed in the previous section, ultraviolet sensitive photomultipliers also retain a significant sensitivity in this region.

In order to avoid this filter leakage problem and to improve sensitivity of an ultraviolet imaging system, Goldman and Marshall

U. S. GOVERNMENT PRINTING OFFICE : 1959 O - 511171
867-100

(1967) have investigated the use of a video camera system featuring an image orthicon tube and a cesium-telluride photocathode (fig. 5). An image orthicon tube permits integration of all elements in the target field simultaneously. This is advantageous because in effect the dwell time for each element is greater than in the line scan system where each element is scanned in sequence. The response of cesium-telluride is negligible at wavelengths longer than 4000Å, and thus would be insensitive to leakage of ultraviolet filters in the red region.

Goldman and Marshall's calculations (1967, p. 11-12) show that the sensitivity of an image orthicon video system is about 25 times more sensitive in the 3000-4000Å region than a line-scanner with a photomultiplier detector. Even in the narrow region between 3000Å and 3200Å, the signal-to-noise ratio would be a very favorable 550:1 for the image orthicon system, whereas only about 20:1 could be expected for a line scanner. However, image orthicons with cesium telluride photocathodes are not available as off-the-shelf items and the costs of producing such a tube and associated circuitry are prohibitive at present levels of funding. Aside from the excessive cost, there is also some question as to whether an image orthicon video system is sufficiently rugged for aircraft operation. There are no further plans for an image orthicon, at least at this time.

Figure 5. Curves showing the quantum efficiencies of the cesium-telluride and cesium-antimony photocathodes, and the spectral transmission of a Corning 7-54 filter.

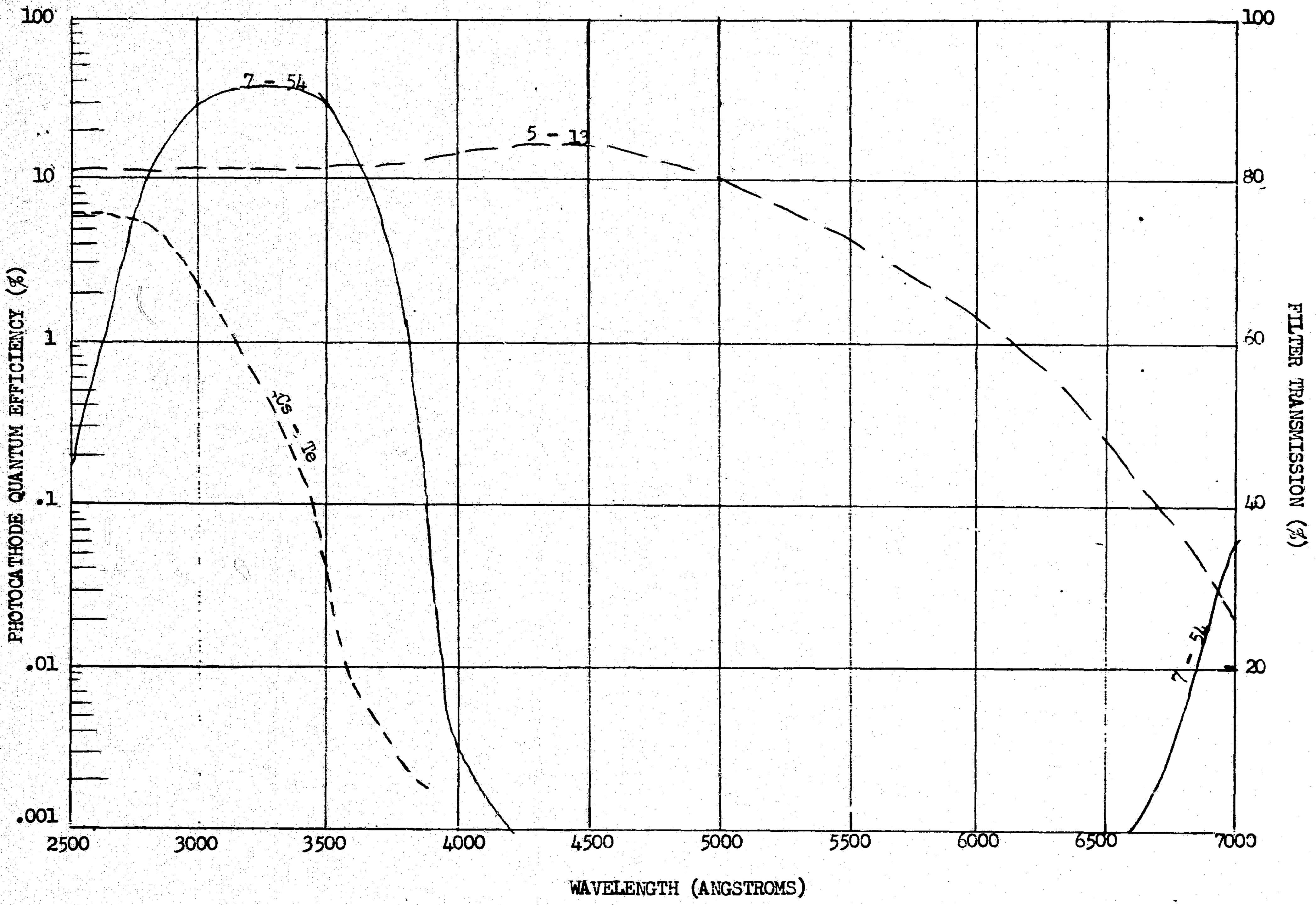

100
10
1
.1
.01
.001
PHOTOCATHODE QUANTUM EFFICIENCY (%)
100
80
60
40
20
FILTER TRANSMISSION (%)
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
WAVELENGTH (ANGSTROMS)
7 - 54
5 - 13
Cs - Te
7 - 54

Figure 5

SPECTRAL STUDIES

Reflectance and luminescence properties of selected rocks from Saudi Arabia and from Indiana.

Spectral measurements were completed by Watts (1967) on 34 rock samples. The samples include two suites: one from Saudi Arabia, and the other from selected limestone quarries in Indiana.

The Saudi Arabian samples, provided by U. S. Geological Survey personnel in that country, include selected andesite and rhyolite rocks because it was hoped that measurement of their reflectance properties would be helpful in distinguishing between them in the field by airborne remote sensing methods. Phosphate samples were also included because it was hoped that ultraviolet stimulated luminescence might be a measurable property that would aid airborne prospecting for this commodity in the northern part of Saudi Arabia.

The Indiana limestone samples were provided by the Geological Survey of Indiana in the hope that laboratory spectral measurements might provide information of direct importance in designing instrumentation capable of distinguishing limestone of varying quality along relatively inaccessible quarry faces.

A Cary Model 14 spectrophotometer and an integrating sphere were used for the reflectance measurements. The source was a hydrogen arc for the ultraviolet region and a tungsten source for the visible region. For the luminescence measurements, A Bausch and Lomb monochromator was place between the xenon-mercury source and the sample; this arrangement was used to limit excitation wavelengths to four bands in the ultraviolet: 2400 to 2700Å, 2600 to 3000Å, 3000 to 3400Å, and 3500 to 3900Å. A Gaertner prism monochromator was place between the sample and the detector and was used to analyze the emitted light from the sample.

Both the limestone and the phosphate sample have relatively high reflectance values and show a significant increase in reflectance with wavelength (fig. 6 and 7). For example, values on the order of 25 percent at 2500Å and 70 percent at 7000Å were observed. Andesite samples (fig. 8) on the other extreme, have essentially flat reflectance curves with values ranging from seven to 15 percent. Rhyolite samples (fig. 9) are generally similar to the andesite although four samples did exhibit a moderate increase at wavelengths longer than 6000Å, where two to four times the spectral reflectance of the andesite was observed, and it may be possible to discriminate some rhyolite outcrops in the field by means of red and infrared photography.

The spectral emission for ultraviolet excited luminescence from the phosphate sample (fig. 10) is broad, commonly exceeding 2000Å at half intensity with an emission maximum at or near 4800Å in the visible. The efficiency of energy conversion appears to be nearly constant for all excitation bands between 2400Å and 3900Å. Analysis of both phosphate luminescence and reflectance data indicates that Fraunhofer line-depth techniques are feasible and that maximum detectivity can be achieved at the K-line of calcium at 3934Å.

The spectral emission for the Indiana limestone samples (fig. 11) is also broad, commonly exceeding 600Å at half intensity with the emission maximum at or near 4000Å. The 2600-3000Å band appears to be more efficient in stimulating luminescence than bands at longer wavelengths. Because this band lies in the so-called "solar-blind" part of the spectrum, distinguishing luminescing limestones could only be accomplished with an active ultraviolet imaging system, such as the Westinghouse prototype described by Hemphill and Carnahan (1965).

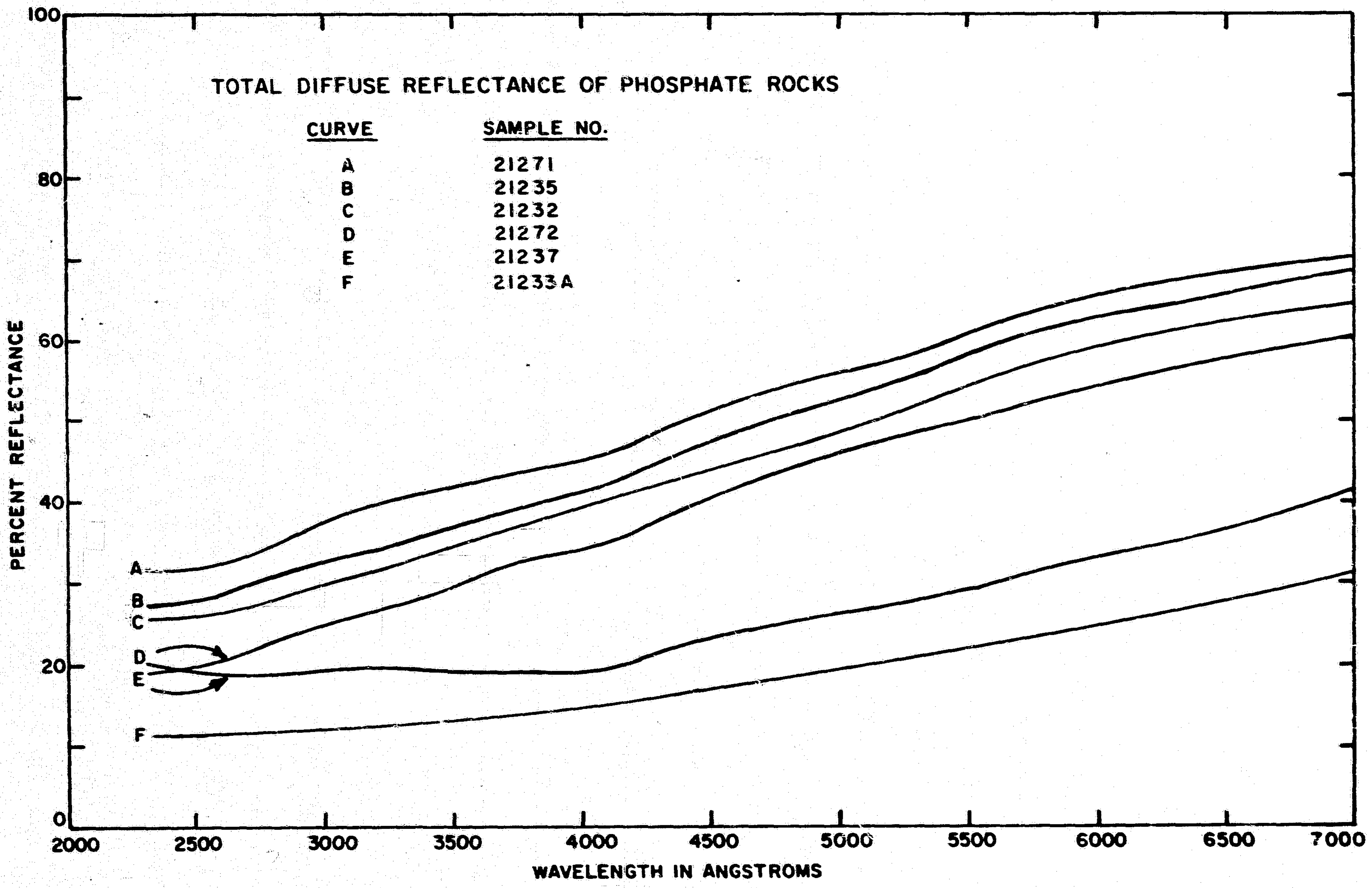


Figure 6. Curves showing diffuse spectral reflectance limestone samples (Watts, 1967).

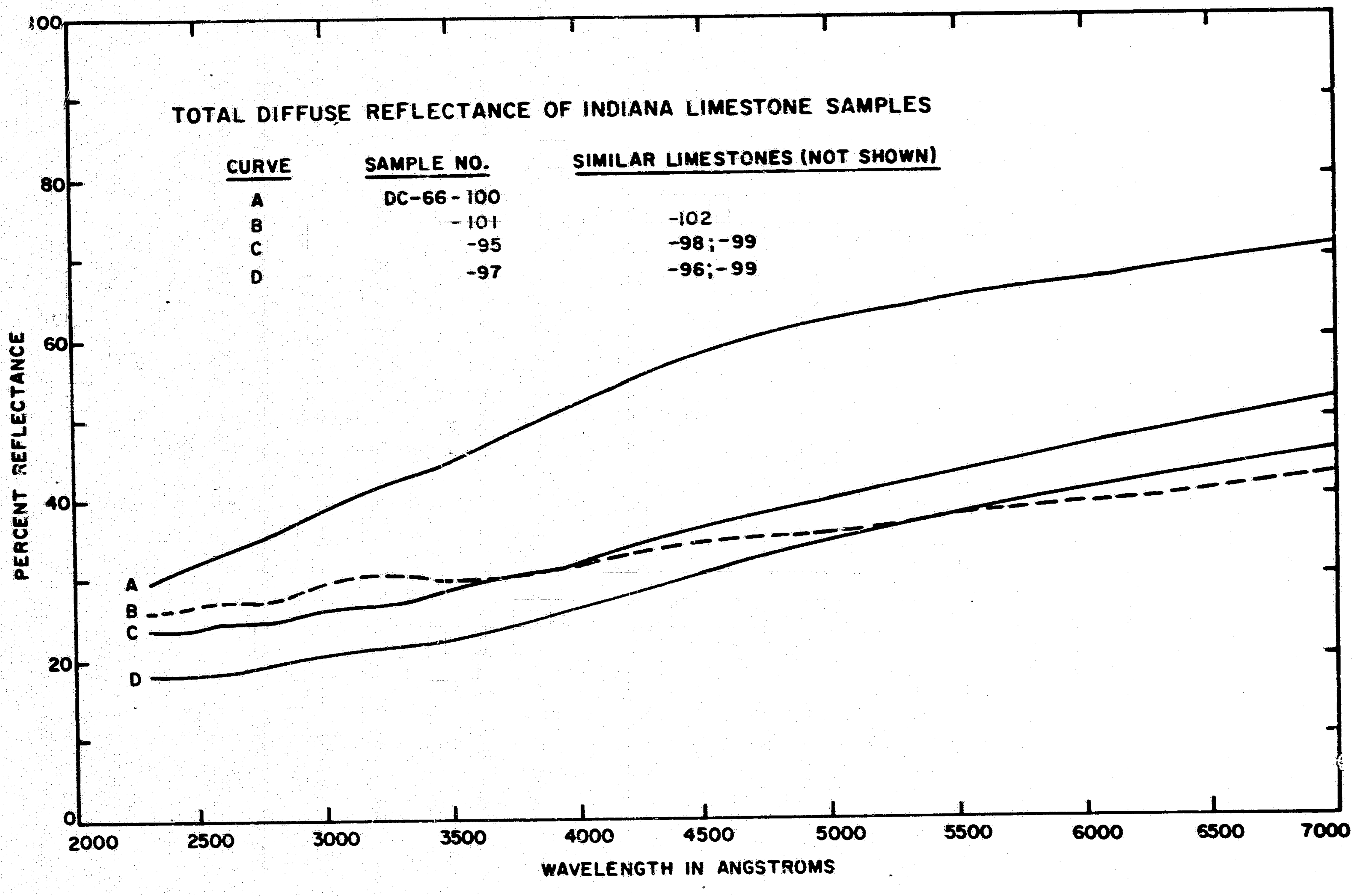


Figure 7. Curves showing diffuse spectral reflectance of limestone samples (Watts, 1967).

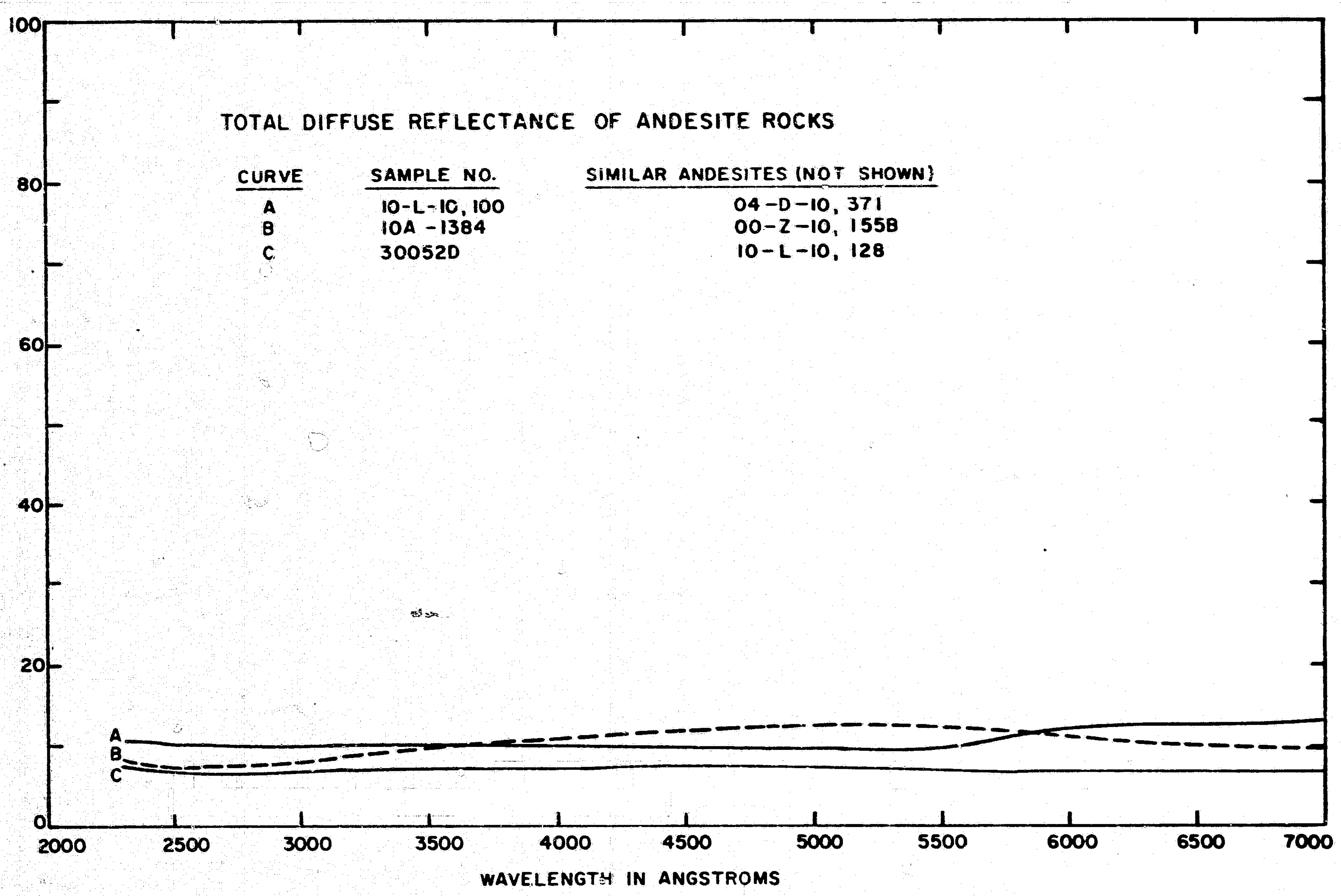


Figure 8. Curves showing diffuse spectral reflectance of andesite samples (Watts, 1967).

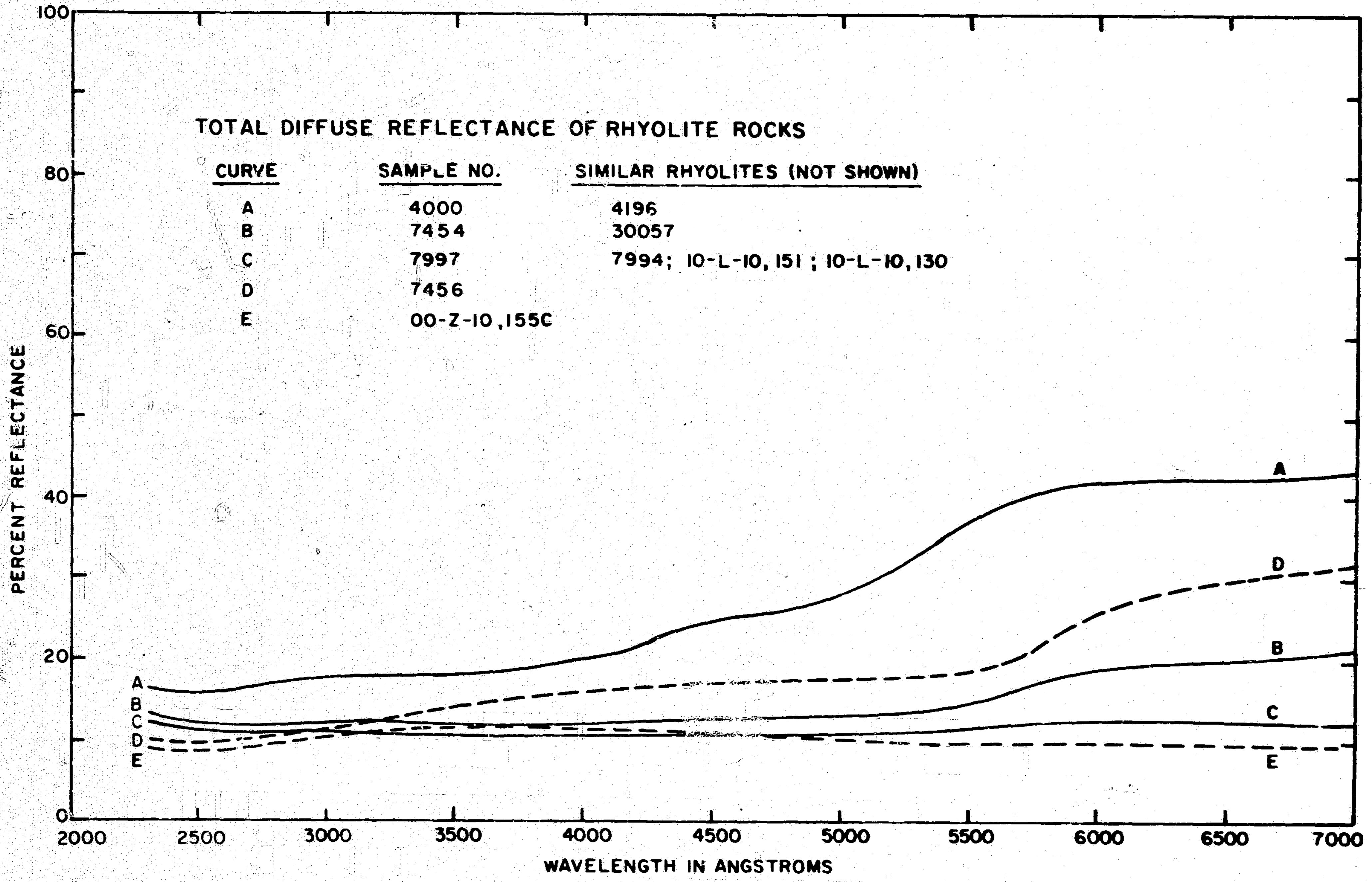


Figure 9. Curves showing diffuse spectral reflectance of rhyolite samples (Watts, 1967).

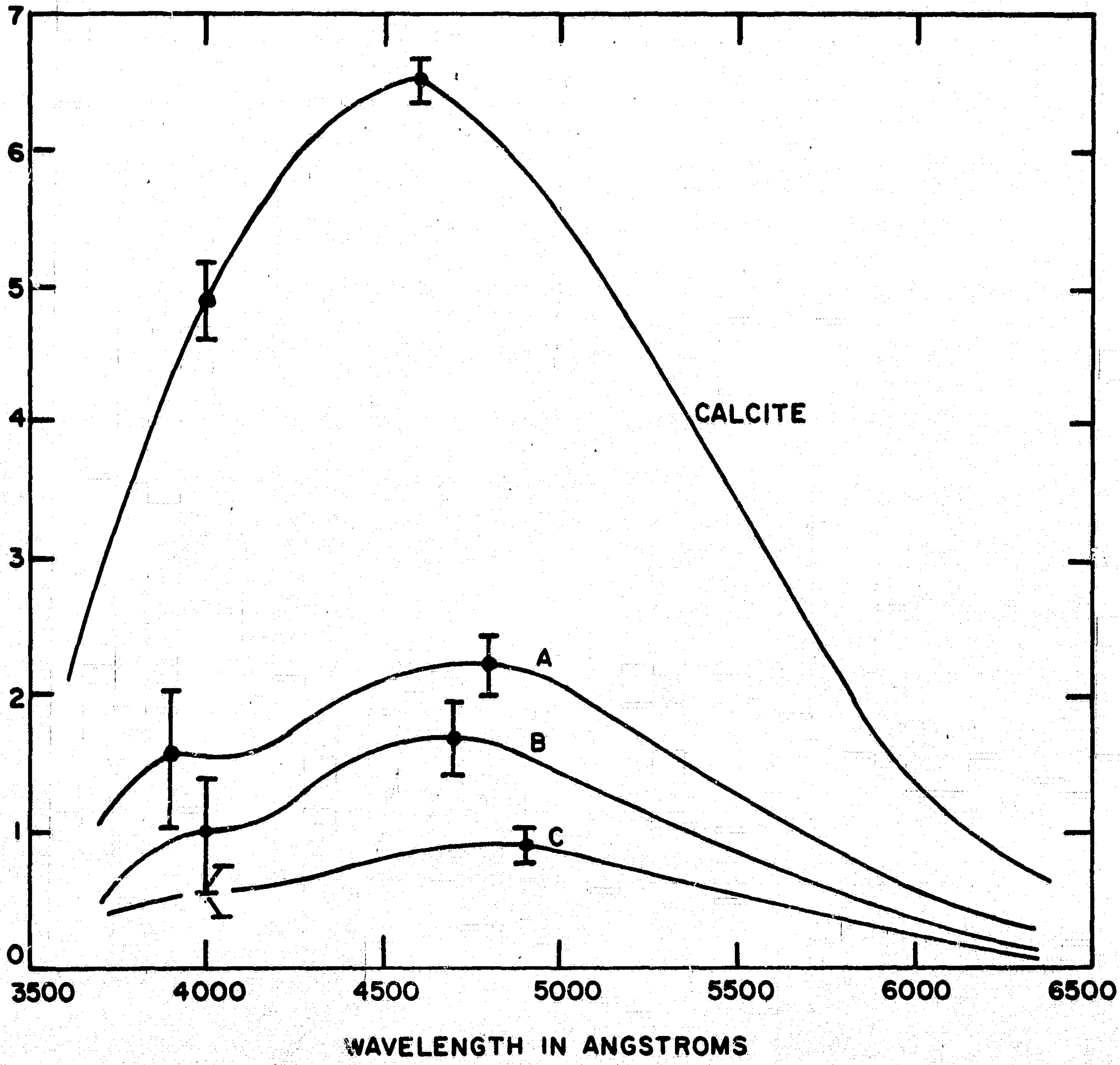


Figure 10. Curves showing ultraviolet excited luminescence emission from three phosphate rocks and a calcite reference (Watts, 1967).

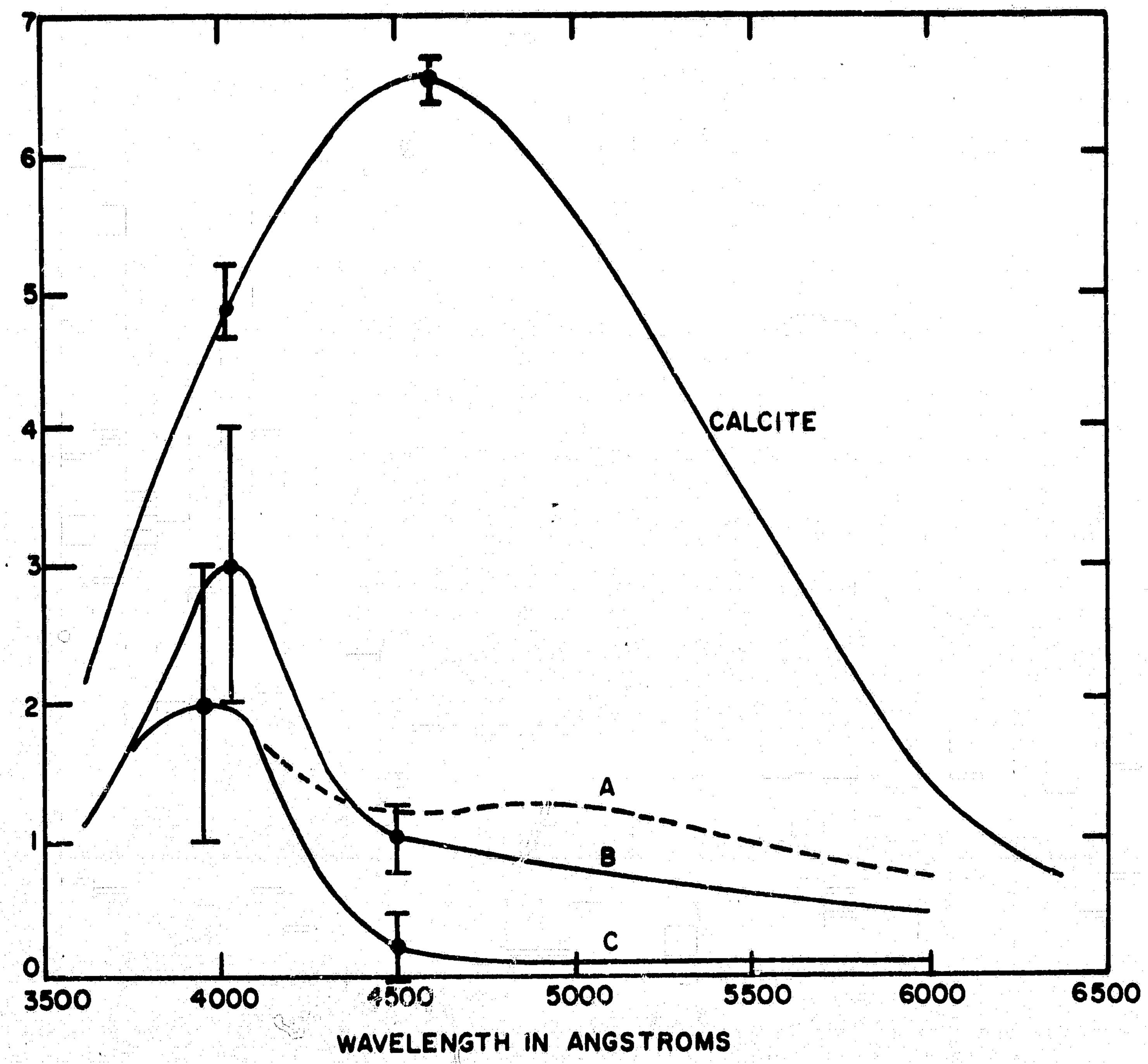


Figure 11. Curves showing ultraviolet excited emission from three limestone samples and a calcite sample (Watts, 1967).

Reflectance and emission measurements in the vacuum ultraviolet

Spectral measurements in the wavelength region between 1000Å and 3000Å 1/ have been completed on 11 rock samples including granite, rhyolite, monzonite, diorite, gabbro, basalt, and dunite (Watts, 1967). These studies were aimed at determining whether there are significant differences in the spectral reflectance and emission properties of these materials which may be used to identify or differentiate them in remote sensing applications. Previous work (Watts, 1966) had suggested that rocks with high silica content (>10%) such as granite and rhyolite show marked increase in reflectance with wavelength, whereas rocks low in silica, such as gabbro and basalt show no appreciable change and are generally independent of wavelength. Previous work also by Watts (1966), and by Thorp, et al (1966) on more than 50 rocks and rock-forming minerals tends to indicate an increase in spectral reflectance at shorter wavelengths. They show that some rocks exhibit an absorption maximum at or near 2500Å but appear to increase spectral reflectance approaching vacuum ultraviolet. However, it was uncertain

---

1/ Remote sensing of natural materials in the so-called vacuum ultraviolet between 1000Å and 1850Å is obviously a lunar oriented application. The early stages of this study were started in 1966 when NASA's AAP feasibility support included lunar applications.

whether this observed property was due to an actual increase in reflectance or whether the increase was caused by ultraviolet stimulated luminescence, unexpected light scattering within the spectrometer, or some other instrument artifact at short wavelengths that is not understood. It was hoped that studies in the region between 1000Å and 1850Å in the vacuum ultraviolet, and 1850-3000Å in the middle ultraviolet would corroborate, or aid in explaining observations made in earlier work.

Spectral reflectance and emission data of polished and ground surfaces of rocks obtained in the recent study are somewhat ambiguous and difficult to interpret. In part, this ambiguity is due to low continuum output of the hydrogen source, as well as other instrumentation problems in the vacuum ultraviolet which make it difficult to separately identify luminescence and reflectance components. In general, however, combined reflectance and luminescence properties of the monzonite and diorite samples are markedly similar, and likewise distinctive from rocks of more acidic and basic composition (fig. 12). Both monzonite and diorite samples exhibit what can be interpreted to be a strong emission peak near 2050Å under vacuum ultraviolet excitation.

Samples of granite, rhyolite, basalt, gabbro, and dunite show spectral curves which are of lower intensity than the monzonite and diorite curves, and without the pronounced peak

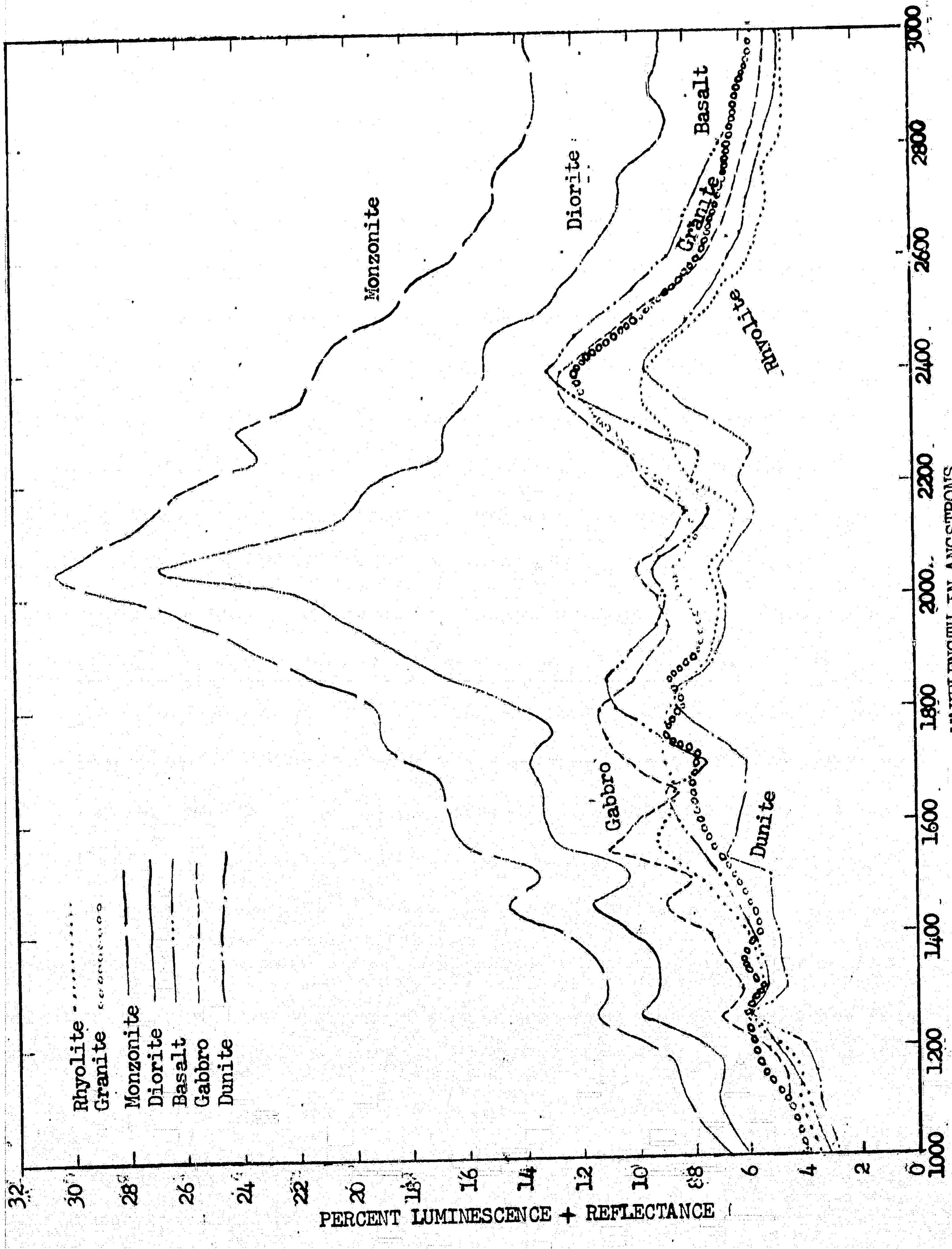


Figure 12. Curves showing combined spectral reflectance and luminescence intensities between 1000Å and 3000Å.

at 2000Å. All of these samples also show a peak near 2400Å. It is interesting to note that this peak approximates a sharp increase in lunar brightness in the 2420-2470Å range reported by the Russians (A.L. Lebedinsky and others, written commun., 1967) from their Zond-3 space probe; significance of this coincidence is not known, however.

According to Watts (1967) there is some evidence in the recent study that sample surface texture is independent of spectral reflectance at wavelengths between 1000Å and 2000Å; in this spectral region Watts observed that both ground and polished surfaces increase in spectral reflectance with wavelength[1]. Spectral reflectance between 2000Å and 3000Å is also observed to increase with wavelength for ground surfaces but to decrease for polished surfaces. Nevertheless, Watts (1966, p. 17) concludes that in general the shape of reflectance curves is independent of sample surface at wavelengths longer than 2300Å and reflectance from both polished and ground surfaces increase from 2300Å to 7000Å.

Further work in the vacuum and middle ultraviolet with a larger variety and number of rock samples and common rock-forming

---

[1] Recent work of Marmo, *et al* (1967) shows that synthetic materials such as quartz, sapphire, and glass actually increase in spectral reflectance at shorter wavelengths in the vacuum ultraviolet. Marmo's data show spectral reflectance to be on the order of 10 percent at 2000Å and 15 percent at 1100Å (45 degree angle of incidence) for these materials.

minerals will be required to verify some of the data obtained in the recent study and to resolve apparent discrepancies with earlier work. However, further work in the vacuum ultraviolet is not justified at this time within the charter of the current ultraviolet project and the "non-lunar" scope of recent NASA funding.

REPORTS COMPLETED DURING THE CONTRACT PERIOD

Goldman, Howard, and Marshall, Robert, 1967, Comparison of a UV scanner/photomultiplier with an image orthicon, U. S. Geological Survey Interagency Report NASA 97.

Watts, H. V., and Goldman, H. J., 1967, Visible and ultraviolet reflectance and luminescence from various Saudi Arabian and Indiana limestone rocks, U. S. Geological Survey Interagency Report NASA 92.

Watts, H. V., and Goldman, H. J., 1967, Vacuum ultraviolet measurements of reflectance and luminescence from various rock samples, U. S. Geological Survey Interagency Report NASA - 96

Betz, Howard, 1967, The remote measurement of Rhodamine B concentration when used as a fluorescent tracer in hydrologic studies, U. S. Geological Survey Interagency Report NASA - 101

REFERENCES CITED

Betz, Howard, 1966, Measurement of luminescence by the Fraunhofer line-depth method: U. S. Geological Survey Technical Letter NASA - 70.

Betz, Howard, 1967, The remote measurement of Rhodamine B concentration when used as a fluorescent tracer in hydrologic studies: U. S. Geological Survey Interagency Report NASA - 101

Goldman, Howard, and Marshall, Robert, 1967, Comparison of an ultraviolet scanner/photomultiplier with an image orthicon: U. S. Geological Survey Interagency Report NASA 97.

Hemphill, W. R., and Carnahan, S. U., 1965, Ultraviolet absorption and luminescence investigations progress report: U. S. Geological Survey Technical Letter NASA - 6.

Ichiye, T., and Plutchak, N. B., 1966, Photodensitometric determination of dye concentration in the ocean; Journ. Limnology and oceanography, V. 11, N. 2, p. 364-370.

Kopal, Zdenek, 1962, Physics and astronomy of the moon: Academic Press, New York, 538 p.

Marmo, F. F., Engelman, A., and Schultz, E. D., 1967, Vacuum ultraviolet surveillance techniques, GCA Corp. interim report No. 2, AD 379842 prepared for Air Force Arionics Lab.

Minnaert, M., Mulders, G. F. W., and Houtgast, J., 1940, Photometric atlas of the solar spectrum from 3612Å to 8771Å with an appendix from 3332Å to 3637Å; Schnabel, Kampert, and Helm, Amsterdam.

Thorpe, A. N., Alexander, C. M., and Senftle, F. E., 1966, Preliminary ultraviolet reflectance of some rocks and minerals from 2000Å to 3000Å: U. S. Geological Survey Technical Letter NASA 37.

Watts, H. V., 1966, Reflectance of rocks and minerals to visible and ultraviolet radiation, U. S. Geological Survey Technical Letter NASA - 32.

Watts, H. V., and Goldman, H. J., 1967, Vacuum ultraviolet measurements of reflectance and luminescence of various rock samples: U. S. Geological Survey Interagency Report NASA 96.

Watts, H. V. and Goldman, H. J., 1967, Visible and ultraviolet reflectance and luminescence from various Saudi Arabian and Indiana limestone rocks, U. S. Geological Survey Interagency Report NASA 92.

9.1267

APPENDIX A

STATEMENT OF WORK

Fraunhofer line-discriminator

- I. General statement
- II. Principle of the line-depth method
- III. Objective
    - A. Initial objective
    - B. Subsequent objectives
- IV. Basic design considerations
- V. Specific design requirements for instrument testing and operation.
    - A. Acceptance tests
        - 1. Stationary test
        - 2. Preliminary aircraft test
    - B. Subsequent testing and operation
        - 1. Laboratory and on-the-ground stationary operation.
        - 2. Light aircraft operation
        - 3. NASA aircraft operation
- VI. Proposal preparation, funding, and delivery considerations
- VII. References

U. S. GOVERNMENT PRINTING OFFICE : 1959 O - 511171
867-100

STATEMENT OF WORK

Fraunhofer line discriminator

I. General Statement

Ultraviolet-stimulated luminescence is a property that is used as an aid in detecting and discriminating between some natural materials. Small hand-carried lamps have been used for many years in the exploration for luminescing minerals such as scheelite ($CaWO_4$), an ore of tungsten. However, these portable ultraviolet sources are low powered and are rarely effective more than a few feet from the outcrop. Also, the work must be conducted at night in order to avoid obscuring ultraviolet-stimulated luminescence by a daytime high solar background. Moreover, ultraviolet sources commonly used are line emitters and may be incapable of stimulating luminescence where their output is low. Heretofore, these operational problems have reduced the application of ultraviolet-stimulated luminescence as a tool for discriminating between luminescent materials.

In the last ten years several workers, notably, Kosyrev (in Kopal, 1962), Dubois (in Kopal, 1962), and Spinrad (1964) have used a suitable technique for detecting luminescence on the lunar surface by means of earth-based spectrometers. Briefly, this method involves observing the ratio of the central intensity of a selected Fraunhofer line to the continuum as reflected from the lunar surface, and comparing it with the ratio of the central intensity of the same line observed in the solar spectrum directly.

Luminescence is indicated where the ratio of the central intensity to the continuum in a reflected lunar spectrum is greater than its solar conjugate.

It is proposed that this technique may be feasible for detection of materials on the earth's surface, which have been stimulated to luminesce by solar energy in the near ultraviolet and visible regions. Phosphate rock, evaporite deposits, some borate minerals, and hydrocarbons luminesce at least in some areas, and may be stimulated by the solar ultraviolet. Rhodamine B, an artificial luminescent dye used as a tracer in river and ocean current studies may also be detectable by the Fraunhofer line-depth method. Important in water pollution would be detection of luminescent detergents and oil slicks in rivers and estuaries.

A significant operational consideration in these possible applications is that the line-depth method permits detection of luminescence during daylight and at greater distances than artificial sources of ultraviolet, such as the low powered hand-carried lamps used in mineral exploration heretofore. Hopefully, a Fraunhofer line discriminator can be designed with adequate sensitivity to detect luminescence from aircraft.

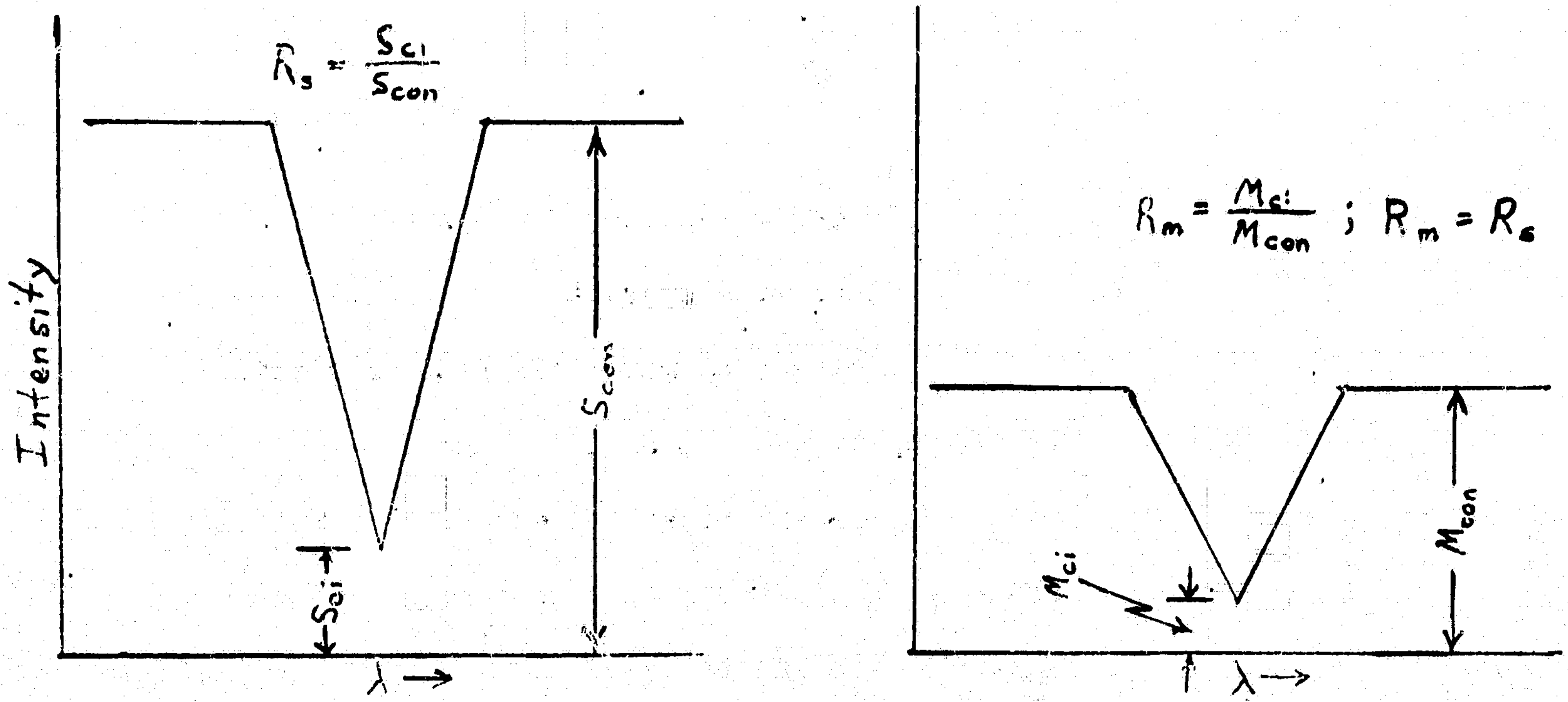
II. Principle of the line-depth method.

The Fraunhofer line-depth method involves observing the ratio of the central intensity of a selected Fraunhofer line to the continuum in the solar spectrum, and comparing it to the ratio of the same line observed reflected (and/or emitted) by a solar illuminated object. Luminescence is indicated only where the ratio in the solar illuminated object exceeds the ratio for the same Fraunhofer line observed in the solar spectrum directly (fig. 1).

Figure 1. Principle of the line-depth method.

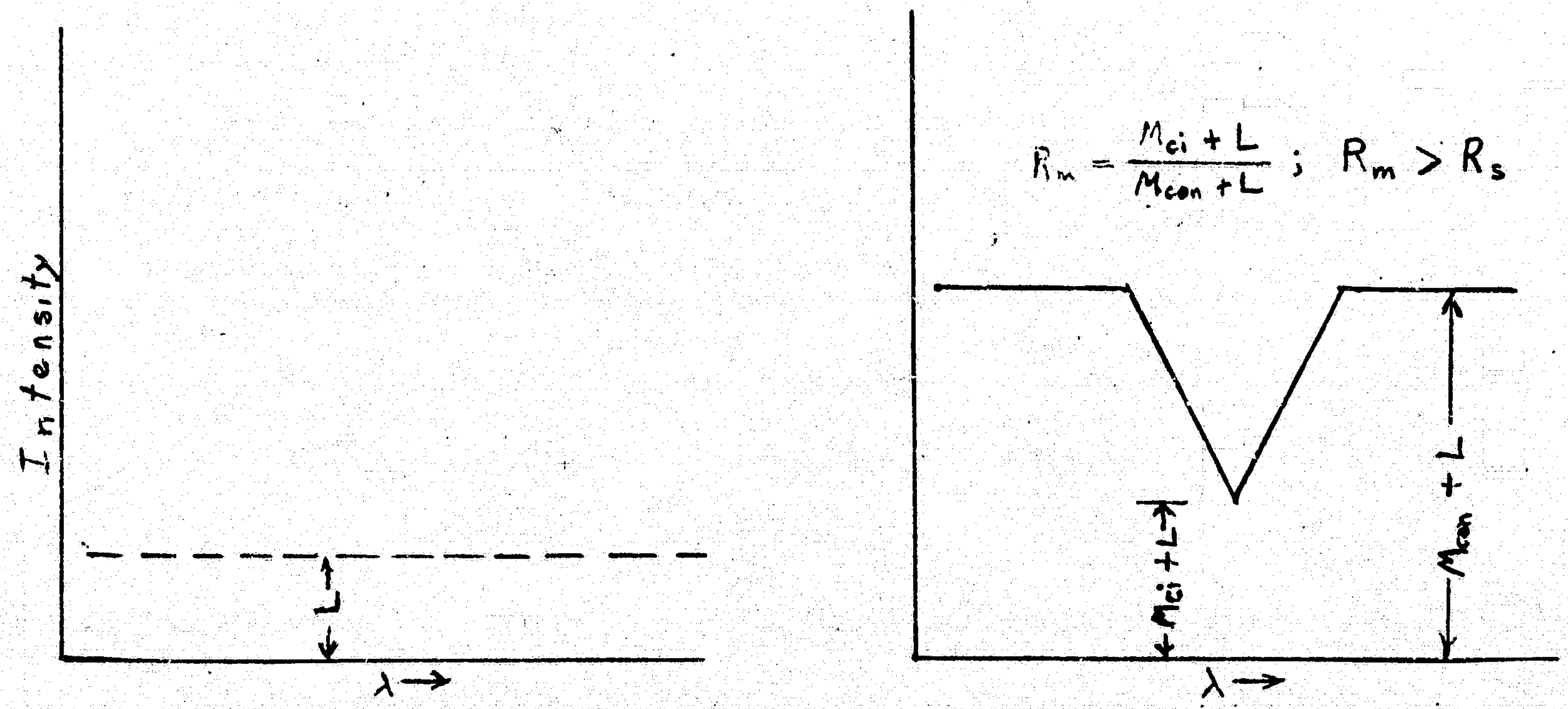
- A. Idealized Fraunhofer line observed in the solar spectrum directly.
- B. Same line profile reflected by non-luminescing material. Although the reflected profile is of lower intensity than the solar profile observed directly, the two ratios are identical; i.e., $R_s = R_m$.
- C. Luminescence contribution; luminescence of most natural materials is sufficiently broad that it can be assumed to be essentially flat in the region of any one Fraunhofer line.
- D. Profile of material which contains both reflected and luminescence components; $R_m \neq R_s$. Amount of luminescence is directly related to lack of correspondence of the two ratios; hence,

$$L = \frac{R_s - R_m}{R_m - 1}$$



A. Line profile, solar spectrum (Observed directly)

B. Line profile of non-luminescing material illuminated by the sun



C. Luminescence contribution

D. Line profile of material containing both reflected and luminescence components

FIGURE 1

III. Objective: To design and build a Fraunhofer line-discriminator suitable for detection of luminescing materials from an aircraft.

A. Initial objective: To discriminate the D_1 and D_2 lines of sodium in order to detect solar stimulated luminescence of Rhodamine B in concentrations of 20 ppb or less in rivers and other natural bodies of water at altitudes of 500 to 1000 feet.

B. Subsequent objectives: To detect solar stimulated luminescence of other natural materials such as phosphate, colemanite, chlorophyll a, and other materials from aircraft using other Fraunhofer lines in the near ultraviolet and visible spectrum as appropriate.

IV. Basic design considerations.

A. In order to conserve funding and time required for contractural negotiation, design, and preliminary performance testing, it is proposed that a single instrument be considered for laboratory and on-the-ground field testing, as well as operation in light aircraft, and final installation in one of the two NASA aircraft.

B. Some components which would be required in aircraft operation, such as automated data handling, might be redundant or unnecessarily complicated during preliminary testing in the laboratory and in the field. Therefore, design of the instrument should emphasize versatility so that components and modifications required in later operational phases can be included as add-on separate cost items. This will permit design refinements to be made as testing proceeds. The instrument in the minimum configuration required for acceptance testing is termed the "basic instrument."

C. The basic instrument will be specifically designed for the detection of Rhodamine B in fresh water at concentrations of 20 ppb or less at distances of 500 feet and a FOV of one degree. Rhodamine B (Udenfriend, 1962) readily lends itself to a quantitative test. For example, dye concentrations can be easily verified by means of conventional laboratory fluorimeters. Also, the D_1 and D_2 lines of sodium (Table 1), where Rhodamine B exhibits peak emission (Udenfriend, 1962), are among narrower Fraunhofer lines and therefore will provide an excellent resolution and sensitivity test of the line discriminator. Moreover, a suitable site for a test, such as a lake, can be more easily located than for certain other luminescent materials.

V. Specific design requirements for instrument testing and operation.

A. Acceptance tests. To be performed by the contractor and assisted by NASA and USGS personnel as appropriate. It would probably be most convenient to conduct acceptance tests at or near contractor's installation provided that suitable facilities are available.

1. Stationary test. Detection of Rhodamine B. Design of basic instrument currently envisioned as suitable for acceptance test is summarized below. Some test parameters such as target distance and instantaneous FOV, which could be difficult to achieve at test location, may be simulated provided both interested USGS and NASA parties concur that simulation is suitable.

   a. Target: Rhodamine B in fresh water at concentrations of 20 ppb.

   b. Fraunhofer line: D_1 and D_2 lines of sodium.

   c. Target distance: 500 feet.

   d. Foreoptics: FOV of one degree, subtending about nine feet at 500 feet.

   e. Scan rate: 30 scans per second. Note: 30 scans per second is the approximate minimal scan rate necessary to maintain an equidimensional FOV during subsequent operations from aircraft moving at 220 feet per second (150 miles per hour) at an altitude of 500 feet.

2. Preliminary aircraft acceptance test. Detection of Rhodamine B in concentrations of 20 ppb from a light aircraft at an altitude of 500 feet above a lake or suitable body of water. Instrument configuration will remain essentially the same as those described for the stationary test. Sole purpose of this test will be to verify satisfactory performance from a moving aircraft, despite aircraft vibration, instrument mounting arrangement, and the aircraft power supply which may be less stable than those available for on-the-ground tests. Design features permitting operational use of the equipment in an aircraft, such as automated data handling and real time read-out of luminescent intensities, will be introduced later in aircraft operation phases (see sections V-B-2 and V-B-3).

Light aircraft to be furnished by NASA or by the USGS. The USGS will assist in placement of dye in the water body and in the collection of supporting information at the test site.

U. S. GOVERNMENT PRINTING OFFICE : 1959 O - 511171
867-100

B. Subsequent testing and operation. To be performed by NASA and USGS personnel as appropriate. Performance of this part of the program will be contingent on successful completion of acceptance tests.

1. Laboratory and on-the-ground stationary operation.
    a. Fraunhofer line to be discriminated: Combined energy from the D_1 and D_2 lines of sodium, plus one other line, probably in the blue or violet, to be selected.
    b. Foreoptics: Design should permit easy installation of appropriate elements which would provide choice of three or four FOVs between 0.5 and 10 degrees.
    c. Scan rate: It would be desirable, although not mandatory, to vary scan rate from one scan/second to 30 scans/second or faster. Scan rate must exceed one scan/second in order to minimize changes in solar flux during the scan period.
    d. Data output can be in either digital form that permits relative intensity of luminescence to be read out directly, or in an analog form from which luminescence intensity can be easily calculated.

2. Light aircraft operation.

a. Fraunhofer lines to be discriminated: Combined energy from the D_1 and D_2 lines of sodium (Rhodamine B), a line in the blue or violet to be selected, and the C line of hydrogen. Filters and/or elements to permit these changes in spectral region are to be made by simple substitution of components.

b. Foreoptics: Same as 1b.

c. Scan rate: To be 30 scans/second in order to minimize ground area integrated during instantaneous FOV (assuming an aircraft speed of 150 miles/hour. Minimal integrated ground area will permit more precise spatial delineation of dye concentration.

d. Data output should be in digital form that permits relative intensities of luminescence to be read out directly in real time, and recorded on a strip-chart recorder.

e. Design must permit calibration of data readout and "peaking" of Fraunhofer line sensitivity (such as against an artificial phosphor standard) to be routinely completed under field conditions. Instrument operation and routine maintainance must be sufficiently simple that they can be completed by personnel with minimal technical background and training.

f. Instrument must withstand vibration commensurate with light aircraft such as the Cessna 180, Beaver, and Twin Beechcraft. Instrument must contain adaptations for adequate shock mounting.

g. Power supply must be readily convertible to aircraft operation, i.e., 28 volts, 400 cycle.

U. S. GOVERNMENT PRINTING OFFICE: 1959 O - 511171
867-100

e. Scan rate cont'd.

Lockheed Electra (ground speed of 360 miles/hour, or 528 feet/second). Scan rate should be 70 scans/second in order to minimize ground area integrated during instantaneous FOV.

VI. Proposal, funding, and delivery considerations.

A. Calculations supporting the feasibility of the proposed equipment to detect Rhodamine B together with conceptual drawings of the line discriminator are to be included in the proposal.

B. Basic instrument used in the preliminary acceptance tests are to be identified separately in the funding profile. All add-on components necessary for modifying FOV, adapting instrument to Fraunhofer lines other than the D_1 and D_2 lines, and to permit aircraft operation, are also to be identified separately.

C. Proposal items are to be graded as follows:

1.	Statement of work coverage	20%
2.	Cost and technical feasibility of approach	50%
3.	Personnel and related experience	20%
4.	Task time	10%

D. Delivery of basic instrument should be within three months after receipt of firm order.

E. Tentative schedule for testing and operation.

1. Acceptance tests (three weeks).
2. Laboratory and on-the-ground stationary operations (six weeks).
3. Light aircraft operation (12 weeks).
   a. Initially Rhodamine B.
   b. Other luminescent materials.
4. Installation and operation from the NASA Convair 240 and Lockheed Electra.

VII. References

A. Kosyrev, K.A., (in Kopal), 1962, "The luminescence of the lunar surface": Physics and astronomy of the moon, Acad. Press, New York, p. 392-394.

B. Dubois, J., (in Kopal), 1962, "The luminescence of the lunar surface": Physics and astronomy of the moon, Acad. Press, New York, p. 392-394.

C. Spinrad, H., 1964, Lunar luminescence in the near ultraviolet: Icarus, v. 3, p. 500-501.

D. Udenfriend, S., 1962, Fluorescence assay in biology and medicine: Acad. Press, New York.

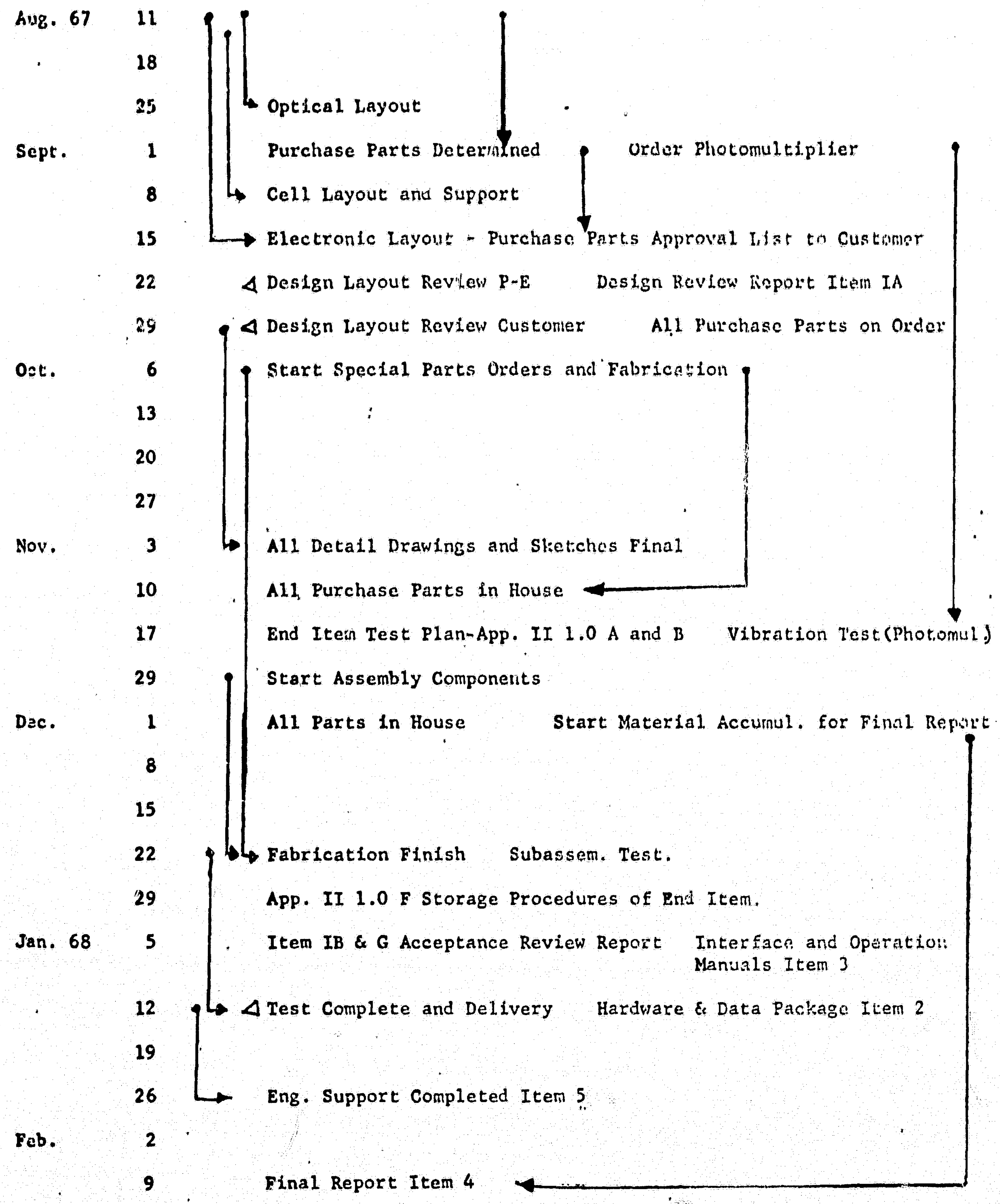
TABLE I

Fraunhofer lines in the near ultraviolet and visible regions of the spectrum, suitable for observation by the line depth method.

Line	Color	Wavelength	Source
A	Deep red	759 Å	Oxygen (Atmosphere)
B	Red	6867Å	Oxygen (Atmosphere)
C	Red-orange	6563Å	Hydrogen
D_1	Yellow	5896Å	Sodium
D_2	Yellow	5890Å	Sodium
F	Blue	4861Å	Hydrogen
G	Violet	4340Å	Hydrogen
H	Deep violet	3968Å	Calcium
K	Deep violet	3934Å	Calcium

APPENDIX B

AIRBORNE F. L. DISCRIMINATOR



Aug. 67	11		
	18		
	25	Optical Layout	
Sept.	1	Purchase Parts Determined	Order Photomultiplier
	8	Cell Layout and Support	
	15	Electronic Layout -	Purchase Parts Approval List to Customer
	22	◁ Design Layout Review P-E	Design Review Report Item IA
	29	◁ Design Layout Review Customer	All Purchase Parts on Order
Oct.	6	Start Special Parts Orders and Fabrication	
	13		
	20		
	27		
Nov.	3	All Detail Drawings and Sketches Final	
	10	All Purchase Parts in House	
	17	End Item Test Plan-App. II 1.0 A and B	Vibration Test (Photomul.)
	29	Start Assembly Components	
Dec.	1	All Parts in House	Start Material Accumul. for Final Report
	8		
	15		
	22	Fabrication Finish	Subassem. Test.
	29	App. II 1.0 F Storage Procedures of End Item.	
Jan. 68	5	Item IB & G Acceptance Review Report	Interface and Operation Manuals Item 3
	12	◁ Test Complete and Delivery	Hardware & Data Package Item 2
	19		
	26	Eng. Support Completed Item 5	
Feb.	2		
	9	Final Report Item 4	